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RESEARCH MEMORANDUM

EFFECTS OF ADDITIVES ON PRESSURE LIMITS OF FLAME PROPAGATION OF PROPANE-AIR MIXTURES

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SUMMARY

Seven additives in 0.5-volume-percent concentration were studied for their effects on the low-pressure limits of flame propagation of propane-air mixtures. The limits were measured in a flame tube of new design. Mixtures containing approximately 2 to 8 percent propane by volume were studied. The limit curves were without lobes on the rich side and were closely related to quenching-distance data measured by the flash-back of a Bunsen flame.

The data were analyzed by means of the experimental curves and the Le Chatelier law governing the flammability limits of mixed fuels.

Ethyl nitrate and chloropicrin were found to be definite promoters of flame propagation in rich mixtures. Chloropicrin and methyl bromide inhibited propagation in lean mixtures; it was concluded that the effect is chemical and that these additives do not act merely as inert gases. None of the additives promoted flame propagation in lean mixtures more than could be explained by the contribution of the additive to the total fuel in the mixture. Methyl bromide increased the minimum pressure for flame propagation and was the only additive that had an appreciable effect on the minimum. Carbon disulfide had a large inhibitory effect on flame propagation in lean mixtures, as defined by deviations from the requirements of Le Chatelier's law.

INTRODUCTION

It has long been considered important to study catalysts for the combustion of fuels. Both positive and negative catalysts are of practical importance: the positive type because they may increase the heat-release rate or widen the range of stable burning, the negative type because they may act as fire-extinguishing agents.

There are experimental data that indicate the existence of such catalytic effects. In the slow (i.e., flameless) combustion of hydrocarbons, the addition of formaldehyde or acetaldehyde to the mixture is found to reduce or to eliminate the induction period of the reaction (ref. 1). In these cases, the additive acts in a positive manner; that is, it promotes the oxidation. On the other hand, hydrogen added to mixtures of propane and higher hydrocarbons in oxygen may act as a negative catalyst; under some circumstances, the hydrogen completely inhibits the slow combustion of these fuels (ref. 1). Many other examples might be cited.

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In the case of fast burning, striking effects of additives are not so numerous. The only agents that have been put to wide practical use are tetraethyl lead to inhibit engine knock, various halogen-containing compounds to extinguish fires, and dopes to improve the performance of Diesel fuels. Many materials have been tested for promoting effects on burning velocity; however, only slight changes were observed, and these were consistent with the calculated changes in equilibrium active-particle concentrations in the flames (ref. 2). The influences of various agents on the composition limits of flammability at atmospheric pressure have also been examined. In one such study, the cases in which the lean limit was broadened could be explained by the added heat-release due to the burning of the additive (ref. 3). Some definite promoting effects on the rich limit were found in the same work. Definite inhibiting effects on the composition limits are shown by some halogen-containing compounds. Methyl iodide, for example, narrows the limits more than would be expected if the additive were merely an inert gas (refs. 3 and 4).

The experiments reported in references 2 to 4 were carried out at atmospheric pressure. There is no certainty that the results would be the same at reduced pressures. In view of the importance of low-pressure burning, particularly in jet-engine combustors, a study of the effects of several selected additives on the low-pressure limits of flame propagation in propane-air mixtures was undertaken at the NACA Lewis laboratory. Low-pressure burning was chosen for study because recent work at the Lewis laboratory has improved the understanding of pressure limits (refs. 5 and 6); it was anticipated that it would be possible to evaluate the results so as to distinguish between the various possible types of additive action.

The effects of seven additives on the pressure limits of propane-air mixtures are reported herein. Each additive was chosen because it had been reported to have some effect on other combustion properties or because of general interest. All the tests were made in a tube 3.73 centimeters in diameter; the effects of tube diameter on pressure limits are described in reference 5. The approximate range of propane concentrations studied was 2 to 8 percent by volume. In all the experiments, the additive constituted 0.5 percent by volume of the total mixture of propane, air, and additive. Propane was used because of the ease of handling and its general similarity in combustion properties to other hydrocarbons. The results of the investigation are interpreted with the aid of the Le Chatelier or mixture rule governing the flammability limits of mixtures (ref. 7).

PROCEDURE

Experimental

Apparatus. - The apparatus was basically the same as that used to study the effect of tube diameter on the pressure limits of propane-air mixtures (ref. 5). As in reference 5, a capacitance spark was used as the ignition source. Three modifications were made in order to carry out the present experiments: (1) A tank was provided for the preparation and storage of additive-air mixtures; (2) a glass appendix, from which liquid additives could be distilled, was attached to the vacuum line; (3) a new design of flame tube was incorporated.

The flame tube used in this investigation resembled those described in reference 5 in that it consisted of an ignition section 8.7 centimeters in diameter and 20 centimeters long attached to a narrower propagation section. The previously described tubes were of all-glass construction, and the two sections were smoothly joined. It is reported in reference 5 that, in a propane-air mixture of a given composition, the flame initiated in the ignition section either propagated into and throughout the length of the narrow tube or was extinguished at its entrance. In this way, it was found that the quenching distance was equal to the tube diameter at the pressure limit for propagation of flame into the tube. It is believed that more precise limits would be obtained with an abrupt transition from the ignition section to the propagation section, in place of the more gradual taper that was present in the one-piece tubes.

The flame tube was accordingly assembled in three parts (fig. 1). The upper end of the ignition section was waxed into an annular groove in the brass adapter. A tapered hole was centered in the adapter to receive the matching taper ground on the lower end of the propagation section. The taper joint was necessary to prevent the tube from sliding into the ignition section when the apparatus was evacuated.

The propagation section itself was a precision-bore, heavy-wall glass tube 3.73 centimeters in diameter and 50 centimeters long. Inasmuch as the flames in these experiments either propagated the length of the tube or were extinguished at its mouth, it was considered unnecessary to use a tube 100 centimeters long.

Preparation of propane-air-additive mixtures. - The propane-air-additive mixtures were prepared by the method of partial pressures; ideal gas behavior was assumed. The pressures of propane, air, and additive were read on a precision absolute manometer with the aid of a cathetometer.

The additives constituted only 0.5 percent of the total mixture by volume. This corresponds to a partial pressure of 3.8 millimeters of mercury in a mixture prepared at a total pressure of 1 atmosphere. Therefore, in order to avoid the possibility of large error in the additive concentration, a 5.0 percent mixture of additive and air was first prepared. This mixture was then admitted to the storage carboy to a partial pressure of 60 millimeters of mercury; propane was added to the desired partial pressure; and finally dried air was let in to bring the total pressure to 600 millimeters. The concentration of additive in the resultant mixture was thus 0.5 percent by volume, based on the total mixture. This procedure could not be followed when chloropicrin (CCl_3NO_2) was added, because it has a low vapor pressure; it was therefore necessary to measure the partial pressure corresponding to 0.5 percent of this additive directly on the manometer. Some precision was thereby sacrificed, but it is believed that the chloropicrin concentration was within ±1.3 percent of 0.5 percent by volume. 3063

The air used to make up the mixtures was passed through Ascarite (to remove carbon dioxide) and Anhydrone (to remove water vapor). The dew point of the dried air was found to be less than -36° F; it therefore contained no more than 0.03 percent water vapor.

The pressure limits of binary mixtures of propane and air and of additive and air were also determined. These mixtures were prepared in the storage carboy according to the procedure described in reference 5.

Experimental procedure. - The tests were carried out in the manner described in reference 5. Most of the pressure limits were established to within ±1 millimeter of mercury. That is, two pressures were found that differed by 2 millimeters, the higher of which permitted flame propagation throughout the 3.73-centimeter tube, whereas the lower caused extinction at the mouth of the tube. The limit recorded was the average of the two pressures.

Very few cases of erratic flame behavior were noted. The ones that were observed occurred with very lean mixtures, in which the flame was sometimes extinguished between the mouth of the 3.73-centimeter-diameter tube and its upper end, and with some rich mixtures of carbon disulfide and air. Even in these cases, however, the reproducibility of the pressure limits was good.

Analysis of Data

A curve of pressure limit for flame propagation in a 3.73-centimeter-diameter tube against volume percent propane in the propane-additive-air mixture was plotted for each additive. A reference curve for binary propane-air mixtures was also determined (fig. 2). In some cases, the mode of action of the additive could be determined by simple comparison of these two curves; the presence of the additive caused a displacement of the curve for ternary mixtures, with relation to the reference propane-air curve. The comparison was facilitated by plotting both curves on a single graph; examples may be seen in figure 3.

In the case of combustible additives, the propane-additive-air mixtures contained 0.5 volume percent more fuel than is indicated by the volume percent of propane. In such mixtures, then, the lean limits would be expected to be broadened, that is, to lie at lower propane concentrations than for propane alone. Conversely, the rich limits should be narrowed, since the added combustible contributes its own oxygen demand in addition to that of propane.

This method of presenting the data permits immediate detection of five types of additive action by simple comparison of the limit curve for mixtures of propane, air, and additive with the curve for propane and air:

(1) If the rich side of the additive curve lies outside (i.e., to the right of) the reference propane-air curve, the additive exerts a definite promoting influence on flame propagation in rich mixtures. This is true whether the additive itself is combustible or not, because even an inert additive should narrow the rich limit by replacing some of the oxygen.

(2) If the additive is combustible and the lean side of the additive curve lies inside (i.e., to the right of) the reference propane-air curve, the additive exerts a definite inhibiting influence on flame propagation in lean mixtures.

(3) If the additive is incombustible and the lean side of the additive curve lies outside (i.e., to the left of) the reference propane-air curve, the additive exerts a definite promoting effect on flame propagation in lean mixtures.

(4) If the presence of the additive increases the minimum pressure for flame propagation as compared with the minimum of the reference propane-air curve, the additive is an inhibitor of flame propagation in mixtures corresponding to the minimum.

(5) Similarly, if the presence of the additive decreases the minimum pressure for flame propagation, the additive acts as a promoter.

In four cases, decision as to the mode of action of the additive cannot be made without further analysis of the data; these cases are:

(6) If the additive is combustible and the lean side of the additive curve lies outside the reference propane-air curve, the additive may be acting either as a promoter or as an added fuel.

(7) If the additive is incombustible and the lean side of the additive curve lies inside the reference curve, the additive may be acting either as an inert gas or as a chemical inhibitor of flame-propagation reactions. 3063

(8) If the additive is combustible and the rich portion of the additive curve lies inside the reference curve, the additive may be acting as added fuel or as a chemical inhibitor.

(9) If the additive is incombustible and the rich portion of the additive curve lies inside the reference curve, the additive may be acting as an inert gas or as a chemical inhibitor.

The instances in which the additive is combustible and causes both lean and rich limits to occur at lower propane concentrations (cases (6) and (8)) were analyzed by means of the law of Le Chatelier, or mixture rule. The object was to determine whether the displacement of the limits could be accounted for wholly by the contribution of the additive to the fuel content of the mixture.

The mixture rule was formulated to deal with the flammability limits of mixed fuels at atmospheric pressure (ref. 7). It states that a simple additive relation exists between the proportions of the fuels in a lean-limit mixture, as expressed in the following equation:

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} = 1 \tag{1}$$

where

n_1, n_2 percentages of each gas in a lean-limit mixture of the two in air, at atmospheric pressure

N_1 percentage of first gas at lean limit in air, at atmospheric pressure

N_2 percentage of second gas at lean limit in air, at atmospheric pressure

The assumptions that the fuels burn similarly and that they do not interfere with one another are inherent in equation (1). The validity of equation (1) has been tested for a large number of mixtures at atmospheric pressure (ref. 7). It has been found that the rich limits as well as the lean limits obey this rule in many instances. However, large deviations are sometimes found, and these are indicative of departure from the assumptions of similar and independent combustion of the two fuels.

In the present work, the mixture rule was applied to the low-pressure limits of flame propagation in propane-air mixtures containing 0.5 percent combustible additive rather than to the flammability limits at atmospheric pressure. In equation (1), n_2 was set equal to 0.5, the additive concentration; and the values of N_1 and N_2 were read from curves of pressure limit against volume-percent propane or additive in air at a given pressure. The expression was solved for n_1, the concentration of propane in a mixture of propane, additive, and air whose pressure limit of flame propagation in a 3.73-centimeter-diameter tube is the specified pressure. The calculated value of n_1 was then compared with the experimentally observed value.

RESULTS

Propane-Air Mixtures

It was first necessary to ascertain whether the pressure limits of propane-air mixtures determined in the modified flame tube agreed with previous results. The curve of pressure limit against volume percent of propane in air is presented in figure 2. It is interesting to note that the curve does not contain irregular lobes on the rich side such as were found in the course of work on the effects of flame-tube diameter on pressure limit (ref. 5). The flame tubes used in the previous investigation differed from the one used in the present investigation in two ways: (1) the propagation section was 100 centimeters long, instead of 50 centimeters; (2) the juncture of the ignition and propagation sections was tapered, instead of abrupt. The same capacitance-spark ignition source was used in both cases.

It should be emphasized that the irregular lobes described in reference 5 do not correspond to the lobes reported in reference 8 and ascribed to the occurrence of cool flames. The cool-flame lobe reported in reference 8 for propane appeared in mixtures richer than 7.2 percent propane by volume (the richest mixture studied in the present work contained 7.28 percent propane). The irregularities shown in reference 5 appeared in mixtures leaner than 7.2 percent propane. It was therefore concluded that the anomalies in reference 5 were probably due to the effects of aerodynamic disturbances on the flame front.

It is not known which of the two modifications in flame-tube design was responsible for the elimination of the irregularities reported in reference 5 and the resulting smooth curve shown in figure 2. In any event, the present curve is similar to curves of fuel concentration against quenching distance measured by the minimum slit width for flash-back of a Bunsen flame (ref. 9). The correspondence of the critical tube diameters for flame propagation, obtained from pressure-limit measurements, and the minimum slit widths of reference 9 is established in reference 5. It is shown that the slit widths are about 0.7 times the critical tube diameters for lean propane-air mixtures. With the present data, this relation is also found to hold for somewhat rich mixtures. The following table shows values of the ratio of minimum slit width for flash-back to critical tube diameter (3.73 cm) at corresponding pressures and propane concentrations.

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Pressure, mm Hg (a)	Propane, percent by volume (a)	Minimum slit width for flash-back, cm (b)	Ratio of minimum slit width to critical diameter
70	3.00	2.45	0.66
52	3.50	2.33	.62
43	[c]4.03	2.47	.66
47	5.00	2.47	.66
54	5.50	2.63	.71

[a]Fig. 2.
[b]Ref. 9.
[c]Stoichiometric.

The values in this table are within the range of values, 0.49 to 0.78, given in reference 10 for the ratios of slit width to tube diameter for flash-back of a Bunsen flame in propane-air mixtures over the same range of concentrations. This result once again emphasizes that the low-pressure limits of flame propagation of propane-air mixtures may be governed by quenching.

Propane-Air-Additive Mixtures

Curves of pressure limit in a 3.73-centimeter-diameter tube against volume percent propane, for the mixtures containing 0.5 volume percent of additive are presented in figure 3. The propane concentration is based on the total mixture. Each curve is accompanied by the curve for propane and air alone, so that the effect of the additive on the low-pressure limits of flame propagation may be readily seen.

Propane, air, and 0.5 percent ethylene. - Figure 3(a) shows the effect of 0.5 percent ethylene on the low-pressure limits of flame propagation of propane-air mixtures. Ethylene was chosen because it was expected to act simply as an added hydrocarbon fuel, and the curve should serve as a basis for comparison to detect promoting or inhibiting effects of other combustible additives. Figure 3(a) shows that, as anticipated, the lean limits are broadened and the rich limits are narrowed by the presence of the added combustible.

Propane, air, and 0.5 percent ethyl nitrate ($C_2H_5ONO_2$). - It has been reported that ethyl nitrate broadens the rich limit of butane in air at atmospheric pressure (ref. 3). Inasmuch as ethyl nitrate is a combustible, it should have the opposite effect, as does ethylene. The oxygen contained in the molecule is not sufficient to oxidize the added ethyl nitrate to carbon monoxide and water, let alone sufficient to provide extra oxygen for the combustion of butane. It must therefore be concluded that ethyl nitrate acts as a flame promoter in rich butane-air mixtures. Figure 3(b) shows that this material also promotes propagation in rich propane-air mixtures at reduced pressures; the pressure-limit curve for propane, air, and ethyl nitrate lies outside the propane-air curve on the rich side.

Propane, air, and 0.5 percent chloropicrin (CCl_3NO_2). - Ashmore and Norrish found that chloropicrin was a sensitizer for thermal explosions of hydrogen-oxygen and hydrogen-chlorine mixtures. Under some circumstances, however, it could also act as an inhibitor, presumably because of the formation of nitrogen oxychloride (NOCl) by decomposition of the chloropicrin at higher temperatures (refs. 11 and 12). Figure 3(c) shows that chloropicrin promotes flame propagation in rich propane-air mixtures; this effect appears to be quite strong. The limits of lean mixtures, on the other hand, fall inside the propane-air curve. In these cases, chloropicrin seems to act as an inert gas or as an inhibitor.

Propane, air, and 0.5 percent hydrogen. - The flammability characteristics of hydrogen as a fuel and as an additive in mixtures at atmospheric pressure are described in reference 7. The composition limits of hydrogen in air at atmospheric pressure are unusually broad, 4.0 to 75 percent by volume. Such an easily flammable fuel might be expected to exert a promoting effect on flame propagation when added to hydrocarbon-air mixtures. Nevertheless, it was found that the effect of added hydrogen on the lean limits of the saturated hydrocarbons methane and ethane at atmospheric pressure is simply that of an added fuel. In the case of the unsaturated compound, ethylene, hydrogen inhibits flame propagation in lean mixtures.

The effects of hydrogen on the limits of propane-air mixtures at reduced pressures are shown by figure 3(d). It is seen that the addition of 0.5 percent hydrogen broadens the limits of lean mixtures slightly, as would be expected if the hydrogen acted as added fuel. In rich mixtures, the additive curve, as drawn, at first lies just outside the propane-air curve, from approximately 4.5 to 6.5 percent propane. In view of the experimental uncertainty in the pressure-limit measurements, it would perhaps be more correct to state that the additive curve virtually coincides with the reference curve in this concentration range. In either case, hydrogen behaves as if it were promoting flame propagation in these mixtures; it is an added fuel and should therefore cause the rich side of the additive curve to fall inside the propane-air reference curve. The additive curve crosses the propane-air curve at about 6.5 percent and lies within it for richer mixtures; that is, the hydrogen behaves as if it were an added fuel in these mixtures. 3063

Propane, air, and 0.5 percent hydrogen sulfide. - Figure 3(e) shows that 0.5 percent hydrogen sulfide affects the pressure limits of propane-air mixtures qualitatively in much the same way as does hydrogen.

Propane, air, and 0.5 percent carbon disulfide. - The appearance of the additive curve in figure 3(f) is qualitatively almost the same as in figures 3(d) and 3(e).

Propane, air, and 0.5 percent methyl bromide. - Recent experiments have shown that 0.5 percent methyl bromide narrows the composition range of flammability at atmospheric pressure in the case of ethylene, methane, and n-hexane (ref. 13). Figure 3(g) shows that the same effect holds with propane-air mixtures at reduced pressures. The entire additive curve lies inside the propane-air curve; this indicates that methyl bromide inhibits flame propagation in both rich and lean mixtures. In addition, the minimum pressure for flame propagation is markedly increased, from 42 to 51 millimeters of mercury. Methyl bromide was the only additive tested that had a definite influence on the minimum of the pressure-limit curve. Under certain conditions, mixtures of methyl bromide and air are capable of propagating flame at atmospheric pressure within narrow concentration limits if a very strong source is provided to ignite the flammable mixtures (ref. 7). Thus, although this additive is capable of acting as an added fuel, the lean side of the curve in figure 3(g) shows that it does not do so in propane-air mixtures.

DISCUSSION

Pressure limits of additive-air mixtures. - The previous section described qualitatively the effects of seven additives on the low-pressure limits of flame propagation of propane-air mixtures. Definite statements as to promoting or inhibiting action were confined to cases in which the rich or lean sides of the additive curves lay to the right of the corresponding limbs of the propane-air reference curve. The instances in which the additive is combustible and causes both lean and rich limits to occur at lower propane concentrations remain to be discussed. It is of interest to determine whether the displacement of the limits can be explained wholly by the contribution of the additive to the fuel content of the mixture. This was done with the aid of the mixture rule, equation (1).

The values of N_1 were obtained from figure 2. The pressure limits of the additives in air had not previously been determined by the present technique; it was therefore necessary to measure them in order to obtain the desired values of N_2. These determinations were made for mixtures of ethylene, ethyl nitrate, hydrogen sulfide, and carbon disulfide in air; the curves of pressure limit against volume percent additive in air are presented in figure 4. With the exception of the ethylene-air curve, the rich sides of the curves are not complete because of physical limitations. In the case of ethyl nitrate, the vapor pressure at room temperature limited the concentration that could be obtained; in some rich mixtures of hydrogen sulfide with air and carbon disulfide with air, ignition difficulties were encountered with the capacitance spark. The two-lobed curve for hydrogen sulfide (fig. 4(c)) was the only one of this type observed in this investigation.

Chloropicrin and methyl bromide were considered nonflammable, and no attempt was made to measure pressure limits.

One pressure limit was determined for a mixture of 6.89 percent by volume hydrogen in air. The limit found was 77 millimeters of mercury. Flames propagating in this lean mixture were virtually nonluminous; they had to be observed in a completely darkened room after the eyes had become somewhat adapted to the darkness. It was also necessary to shield the eyes from the brilliant flash of the ignition spark. The lean limit of hydrogen in air at 1 atmosphere is 4.0 percent (ref. 7). The pressure limit of 30 percent hydrogen in air in a 3.73-centimeter-diameter tube was estimated from the quenching-distance data of reference 1 by use of the relation between quenching distance and critical tube diameter for flame propagation pointed out in reference 5. This limit was estimated to be 7 to 8 millimeters of mercury. In view of the experimental difficulties in the measurement of hydrogen-air pressure limits, the matter was not pursued further, and these three points were taken to define the pressure-limit curve in an approximate fashion. The data are summarized in the following table:

Hydrogen in air, percent by volume	Pressure limit in 3.73-cm-diam. tube, mm Hg
4.0	760 (ref. 7)
6.89	77 (measured)
30	7-8 (estimated from data of ref. 1)

Comparison of calculated and observed pressure limits of propane, air, and 0.5 percent additive. - The observed pressure limits of propane-air-additive mixtures are compared in figure 5 with those calculated by the mixture rule. The calculated limits are shown by the solid curves. The observed limits are shown by the curves of figure 3 which are inserted as dashed lines for comparison. The calculated limit curves were constructed from values of n_1, the percent propane in the lean-limit mixture of propane, air, and 0.5 percent additive, calculated by means of equation (1). Comparison of the lean sides of the calculated curves with the observed limits in figures 5(a) to (d) shows that the mixture rule holds quite well at reduced pressures for lean-limit mixtures of propane and air containing 0.5 percent by volume ethylene, ethyl nitrate, hydrogen, or hydrogen sulfide. The best agreement between experiment and the predictions of the mixture rule is shown by the mixtures containing ethyl nitrate or hydrogen. The curves for the observed pressure limits of lean mixtures containing ethylene or hydrogen sulfide lie uniformly just inside the calculated curves. The deviations in limit concentration are small along the more vertical portions of the curves and become fairly definite near the minimum (figs. 5(a) and (d)). Some slight inhibitory action of ethylene and hydrogen sulfide on flame propagation in lean propane-air mixtures may be indicated. However, none of the four additives had any striking effect, either of promotion or inhibition; and the broadening of the lean limits noted in figures 3(a), (b), (d), and (e) is seen to be very nearly explainable by the contribution of the additives to the fuel content of the mixtures.

The observed and predicted limits of lean mixtures of propane, air, and 0.5 percent carbon disulfide are compared in figure 5(e). The experimental curve lies far within the predicted curve; the addition of 0.5 percent by volume carbon disulfide thus appears to have a strong inhibitory effect on the pressure limits of lean propane-air mixtures. The limits of mixtures of carbon disulfide with ether, benzene, acetone, and acetaldehyde at atmospheric pressure do not obey the mixture rule (ref. 7).

The magnitude of the inhibitory effect of carbon disulfide may be determined with the aid of the mixture rule. Values of n_1, the percent propane in lean-limit mixtures of propane, air, and 0.5 percent carbon disulfide, were read from the pressure-limit curve, figure 3(f). These values were used to compute the sum $\frac{n_1}{N_1} + \frac{n_2}{N_2}$. According to equation (1), this sum equals unity if the mixture behaves ideally. If the sum is greater than unity, inhibition is indicated in the case of lean-limit mixtures; that is, the limit mixture must contain more propane than predicted by the mixture rule in order for the flame to propagate. In order to emphasize that carbon disulfide has an inhibitory effect in lean propane-air mixtures, the values of the sum were subtracted from unity to give negative numbers.

On the assumption that the slight but uniform discrepancies between calculated and observed lean limits shown by ethylene and hydrogen sulfide (figs. 5(a) and (d)) indicate inhibition, the preceding calculation was also carried out for these two additives. The results are summarized in table I. Ethylene and hydrogen sulfide are seen to inhibit flame propagation at reduced pressures in lean mixtures to the extent of 3 to 4 percent. The inhibition due to carbon disulfide is much larger, of the order of 20 percent.

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Reference 14 reported that 0.5 percent hydrogen sulfide in propane-air mixtures inhibited the maximum burning velocity by about 3 percent; the effect was evaluated by means of a mixture rule analogous to the one used in this investigation. In the case of this additive, therefore, the effects on both combustion properties are in accord. However, reference 14 showed that 0.5 percent ethylene in propane-air mixtures did obey the mixture rule; the present results do not agree with this conclusion. On the other hand, recent studies of the stability of flames in mixtures of propane, ethylene, and air indicated that the mixture rule is not always obeyed by these fuels (ref. 15). A slight suggestion of inhibition was reported. The possible significance of the calculated inhibitory effects of ethylene and hydrogen sulfide, as presented in table I, therefore remains in doubt.

Ethylene and hydrogen sulfide were the only two additives for which the necessary data were obtained to test the application of the mixture rule to rich mixtures. Figures 5(a) and (d) show that the predicted rich limits correspond to the experimental ones reasonably well in view of the fact that the mixture rule was originally intended to apply to lean limits.

No attempt was made to calculate the pressure-limit curves in the region close to the minimum, because of two difficulties: (1) The minimums of the propane-air and additive-air limit curves did not occur at the same pressure; (2) the minimums did not occur at the same percentage of stoichiometric. Therefore, uncertainty existed as to the proper values of N_1 and N_2 to choose for the calculation.

<u>Evaluation of effects of chloropicrin and methyl bromide on pressure limits of propane-air mixtures</u>. - Figures 3(c) and (g) show that chloropicrin and methyl bromide, respectively, have a definite inhibitory effect on the pressure limits of lean propane-air mixtures, since the lean sides of the curves for these additives lie to the right of the reference propane-air curve. It seems reasonable to assume that both of these additives may be considered incombustible; thus, their action cannot be due to a greater affinity for oxygen than propane possesses. Two possibilities remain:

(1) The additive may act simply as an inert gas that replaces part of the oxygen in the mixture.

(2) The additive may act in a specific chemical manner to inhibit the combustion reactions of propane.

The first of these possibilities was checked by measuring the pressure limits in propane-air mixtures containing 0.5 percent inert gas. Pure nitrogen (99.9 percent) was chosen. The results are presented in figure 6, together with the reference propane-air curve. It will be seen that the added nitrogen has no appreciable effect on the pressure limits of any mixture studied. The curves for propane, air, and 0.5 percent chloropicrin and for propane, air, and 0.5 percent methyl bromide are also reproduced in figure 6. Comparison shows that the effects of these additives are much greater than that of nitrogen. It might be argued that the heat capacities of chloropicrin and methyl bromide are considerably greater than the heat capacity of nitrogen, so they should be more effective inerts. However, in view of the low additive concentration, it is believed that this is an unimportant consideration. It is therefore concluded that chloropicrin acts in a specific chemical manner to inhibit flame propagation at reduced pressures in lean propane-air mixtures (although it is a promoter in rich mixtures); methyl bromide has a chemical inhibitory effect in both lean and rich mixtures.

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SUMMARY OF RESULTS

Seven additives in 0.5-volume-percent concentration were studied to determine their effects on the low-pressure limits of flame propagation of propane-air mixtures, with the following results:

1. Of the seven additives tested, none was found to promote flame propagation in lean mixtures at reduced pressure more than could be explained by the contribution of the additive to the total fuel in the mixture.

2. No additive was found that significantly lowered the minimum pressure for flame propagation.

3. Two additives - ethyl nitrate and chloropicrin - were definite promoters of flame propagation in rich propane-air mixtures.

4. Of the combustible additives tested, ethylene and hydrogen sulfide appeared to inhibit flame propagation in lean mixtures to a slight degree. Carbon disulfide was a marked inhibitor.

5. Both chloropicrin and methyl bromide inhibited flame propagation in lean mixtures. Methyl bromide also increased the minimum pressure for flame propagation and inhibited propagation in rich mixtures. The effects were too large to explain in terms of dilution by an inert gas.

CONCLUSIONS

The following conclusions may be drawn from this study:

1. The Le Chatelier law may be applied to the limits of flame propagation at reduced pressures for some mixed fuels.

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2. Chloropicrin has a chemical inhibitory action on flame propagation in lean propane-air mixtures at reduced pressures, even though it is a promoter in rich mixtures. Methyl bromide is a chemical inhibitor in both lean and rich mixtures.

3. Carbon disulfide inhibits flame propagation in lean propane-air mixtures to the extent of about 20 percent, as shown by deviations from Le Chatelier's law.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
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CW-3

TABLE I. - INHIBITORY ACTION OF THREE ADDITIVES ON PRESSURE LIMITS OF LEAN MIXTURES OF PROPANE, AIR, AND 0.5 PERCENT ADDITIVE BY VOLUME

Pressure, mm Hg	Additive		
	Ethylene, $1-\left(\frac{n_1}{N_1}+\frac{0.5}{N_2}\right)$	Hydrogen sulfide, $1-\left(\frac{n_1}{N_1}+\frac{0.5}{N_2}\right)$	Carbon disulfide, $1-\left(\frac{n_1}{N_1}+\frac{0.5}{N_2}\right)$
150	-0.04		
140	-.04		
130	-.03	-0.03	
120	-.03	-.03	
110	-.02	-.03	
100	-.02	-.04	-0.22
90	-.02	-.04	-.22
80	-.02	-.04	-.21
70	-.03	-.03	-.21
60	-.04	-.03	-.21
50	-.07	-.06	-.20

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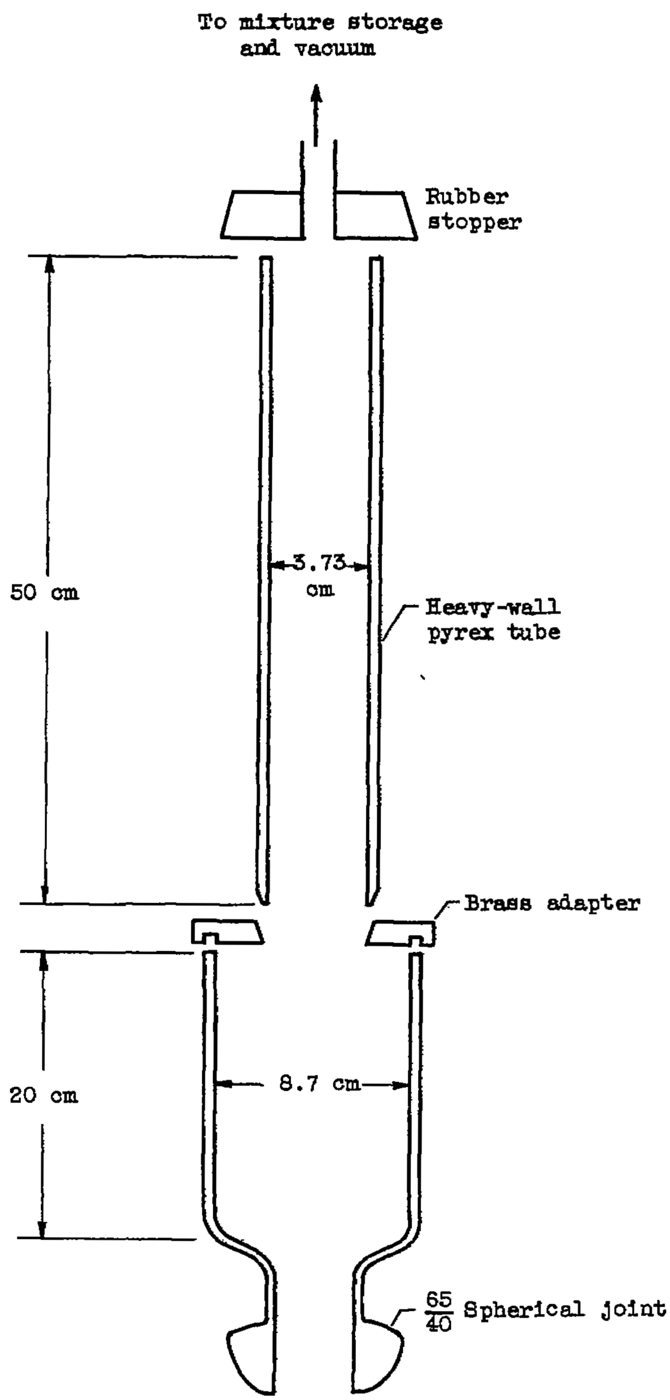

Figure 1. - Flame tube for measurement of low-pressure limits of flame propagation.

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CW-3 back

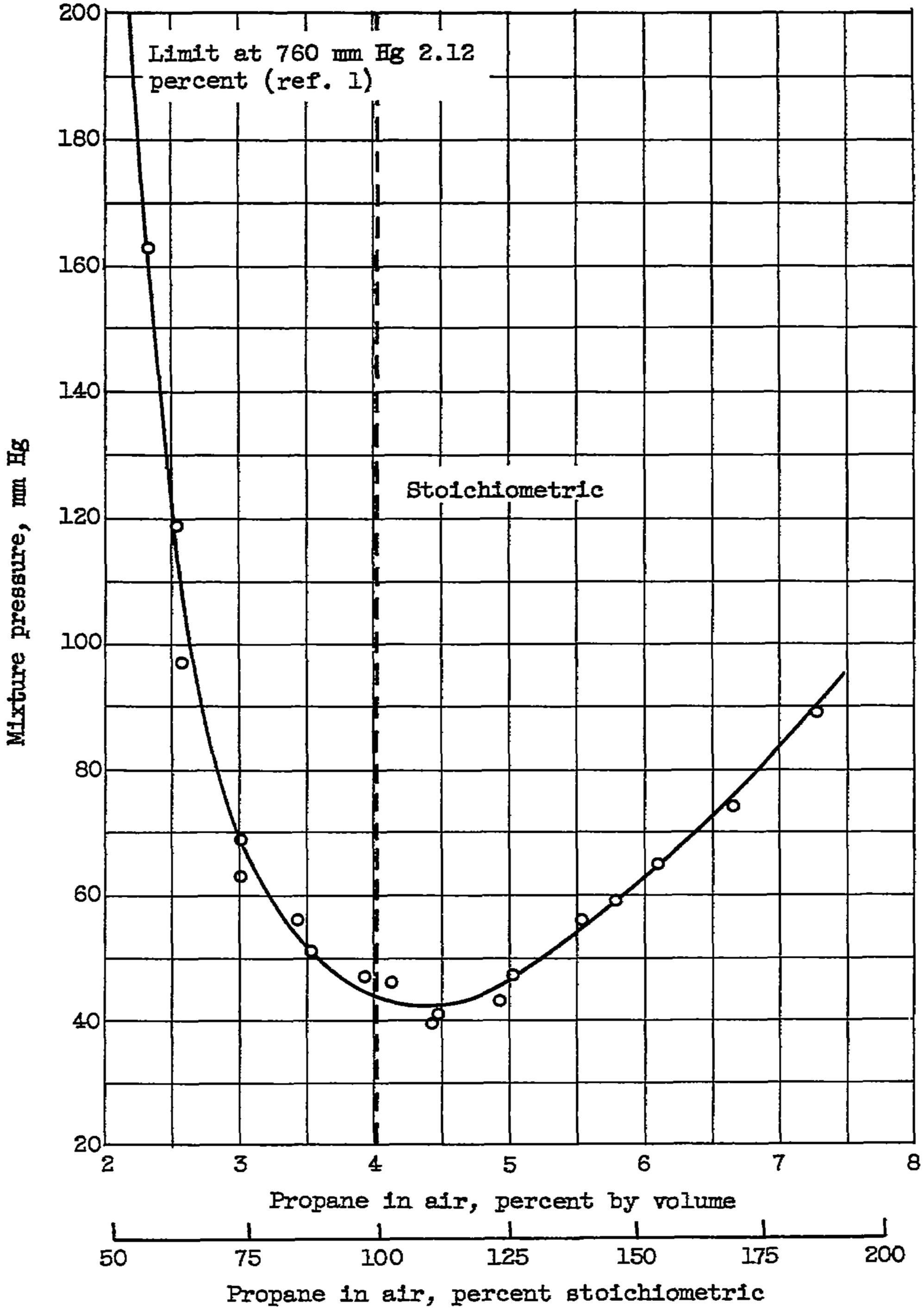

Figure 2. - Pressure limits of flame propagation of propane-air mixtures in 3.73-centimeter-diameter tube.

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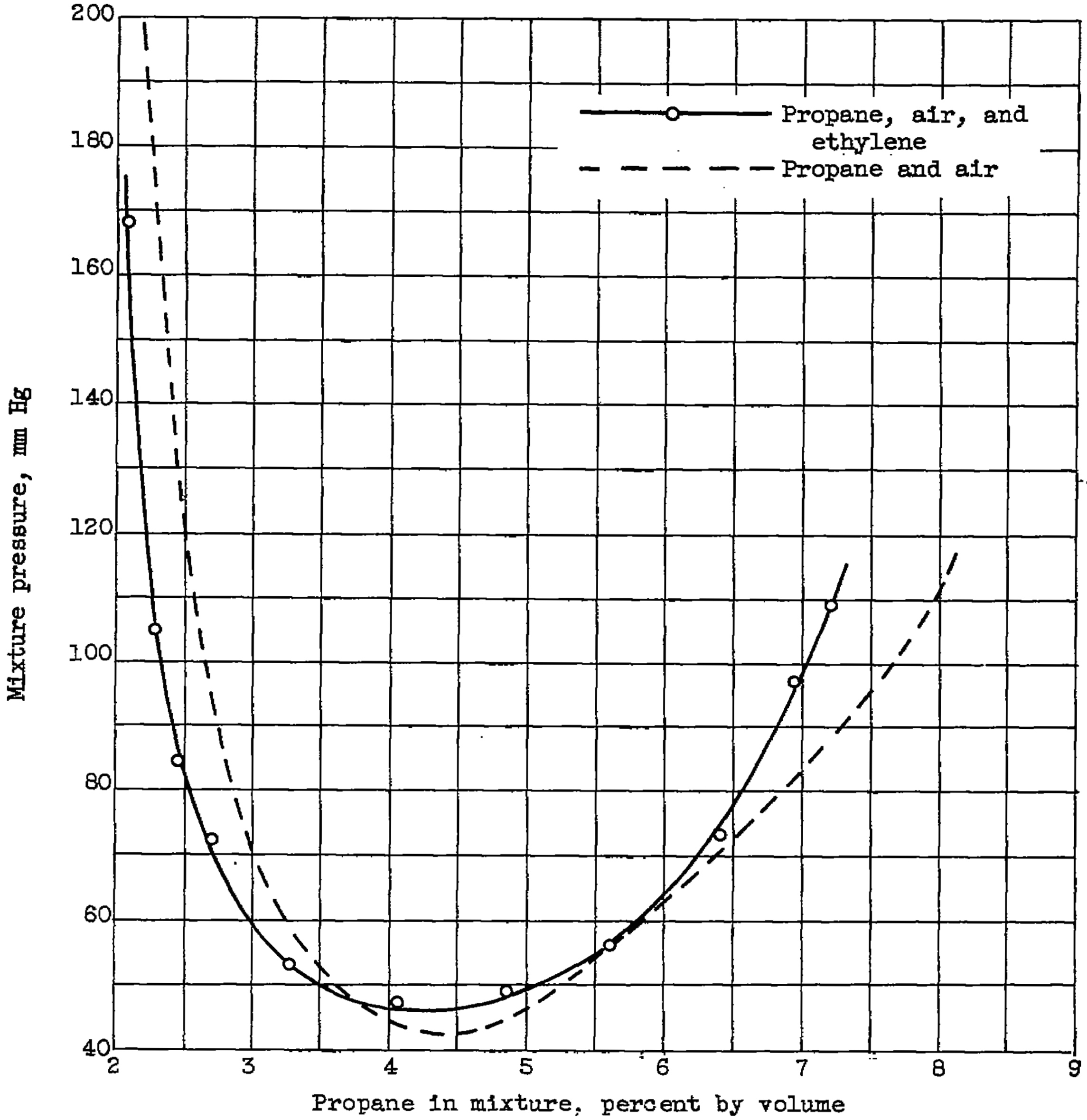

(a) Ethylene, 0.5 volume percent.

Figure 3. - Effects of additives on low-pressure limits of flame propagation in propane-air mixtures in 3.73-centimeter-diameter tube.

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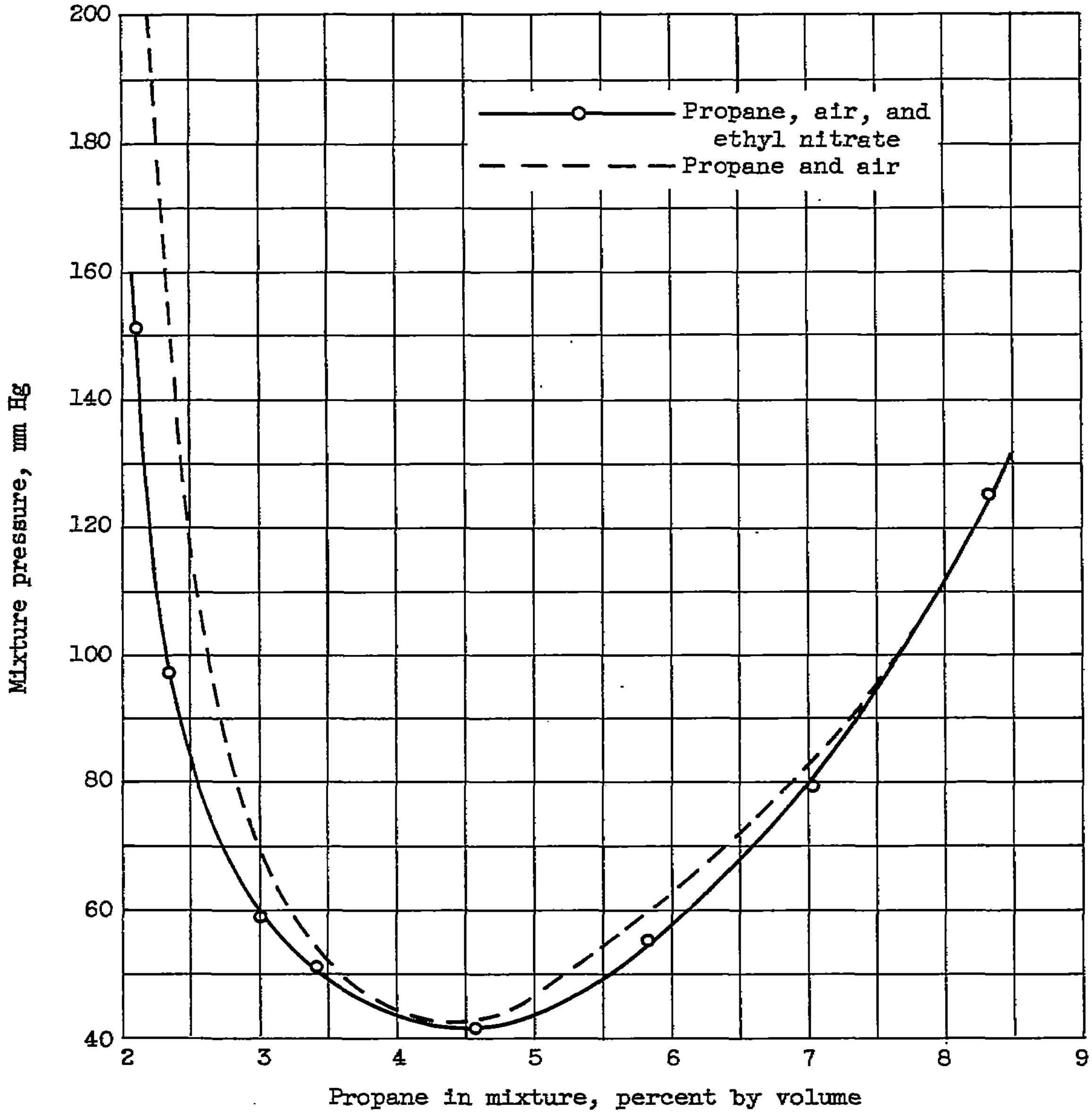
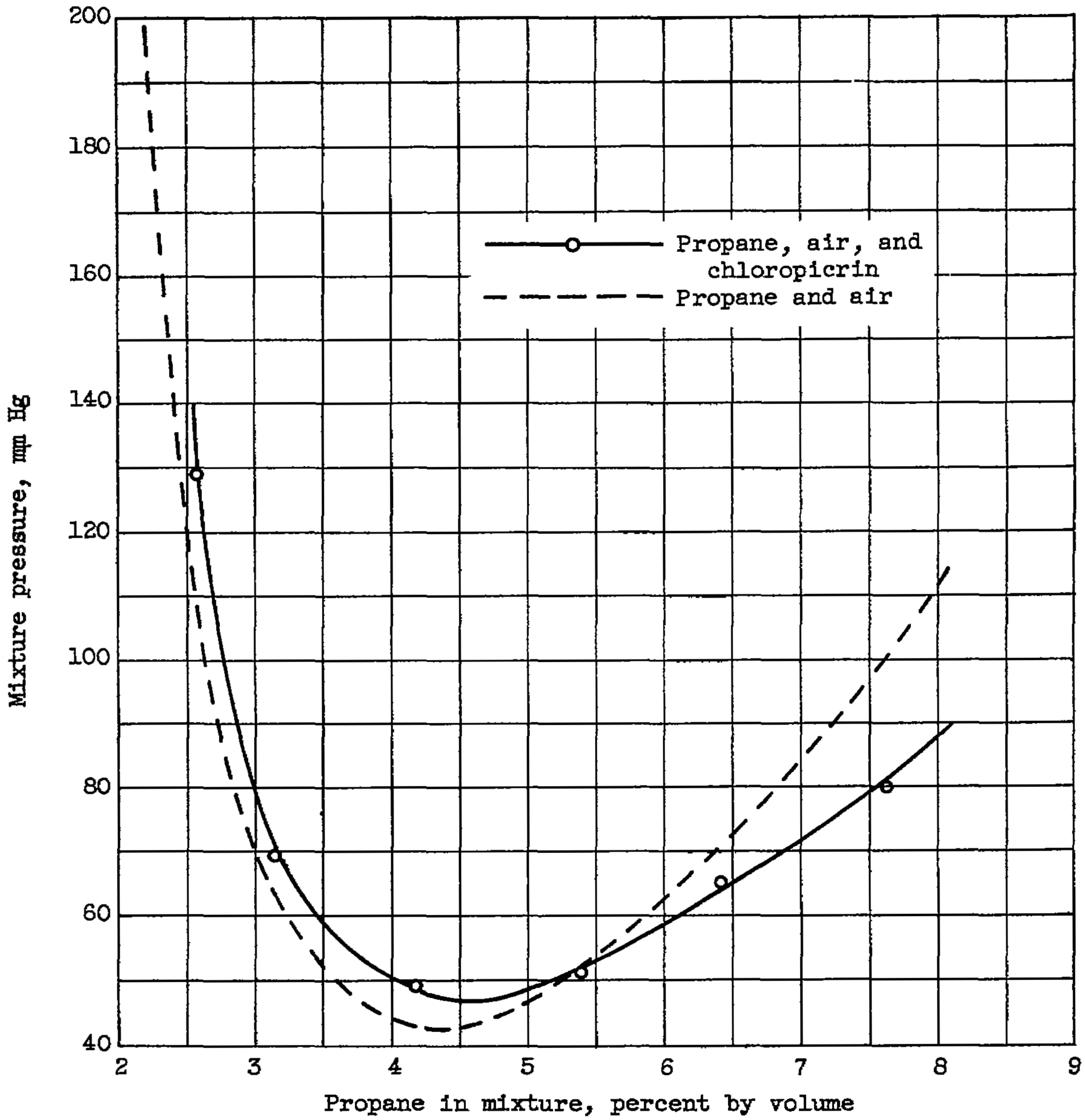


(b) Ethyl nitrate, 0.5 volume percent.

Figure 3. - Continued. Effects of additives on low-pressure limits of flame propagation in propane-air mixtures in 3.73-centimeter-diameter tube.



(c) Chloropicrin, 0.5 volume percent.

Figure 3. - Continued. Effects of additives on low-pressure limits of flame propagation in propane-air mixtures in 3.73-centimeter-diameter tube.

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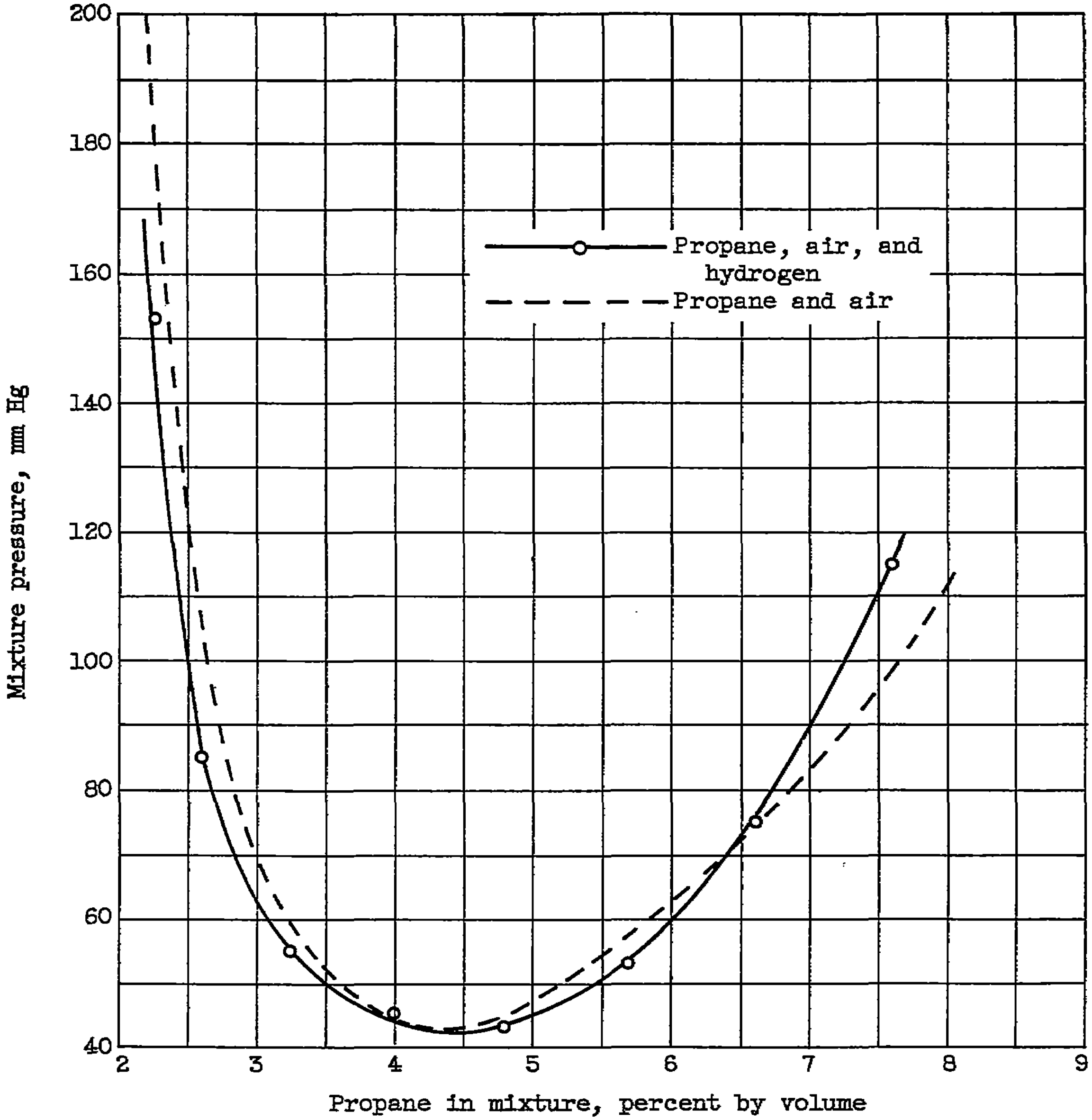
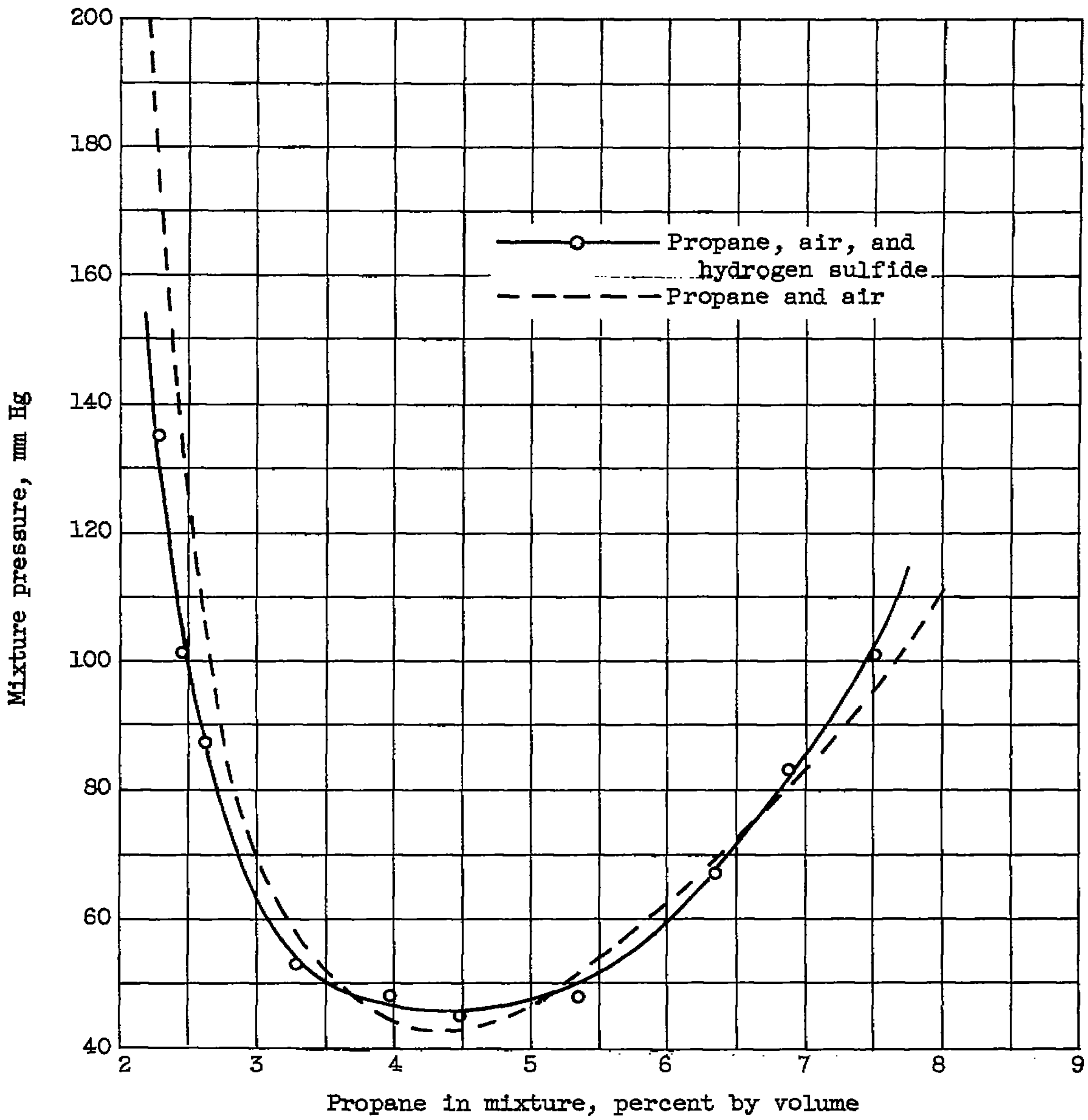


(d) Hydrogen, 0.5 volume percent.

Figure 3. - Continued. Effects of additives on low-pressure limits of flame propagation in propane-air mixtures in 3.73-centimeter-diameter tube.



(e) Hydrogen sulfide, 0.5 volume percent.

Figure 3. - Continued. Effects of additives on low-pressure limits of flame propagation in propane-air mixtures in 3.73-centimeter-diameter tube.

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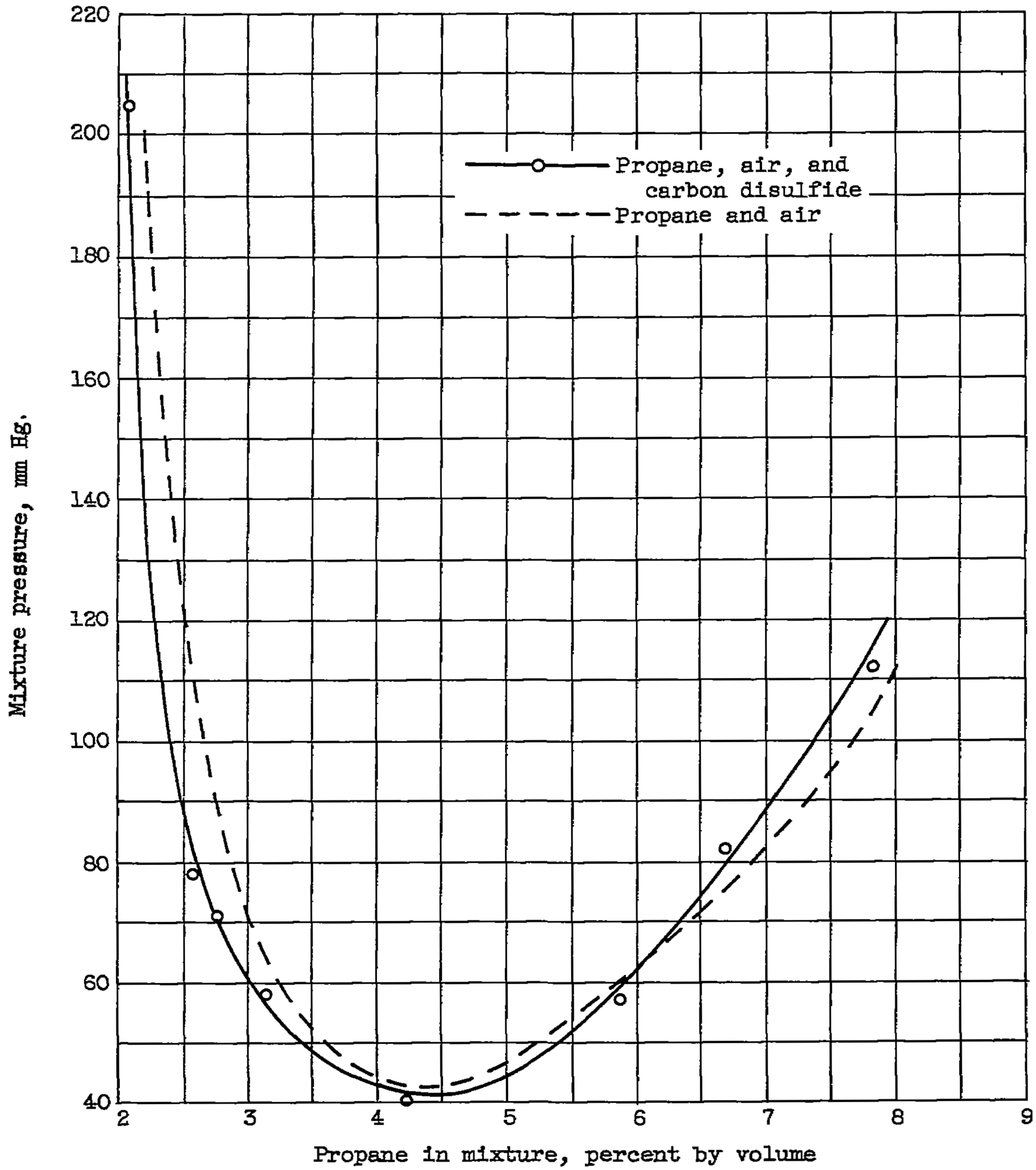
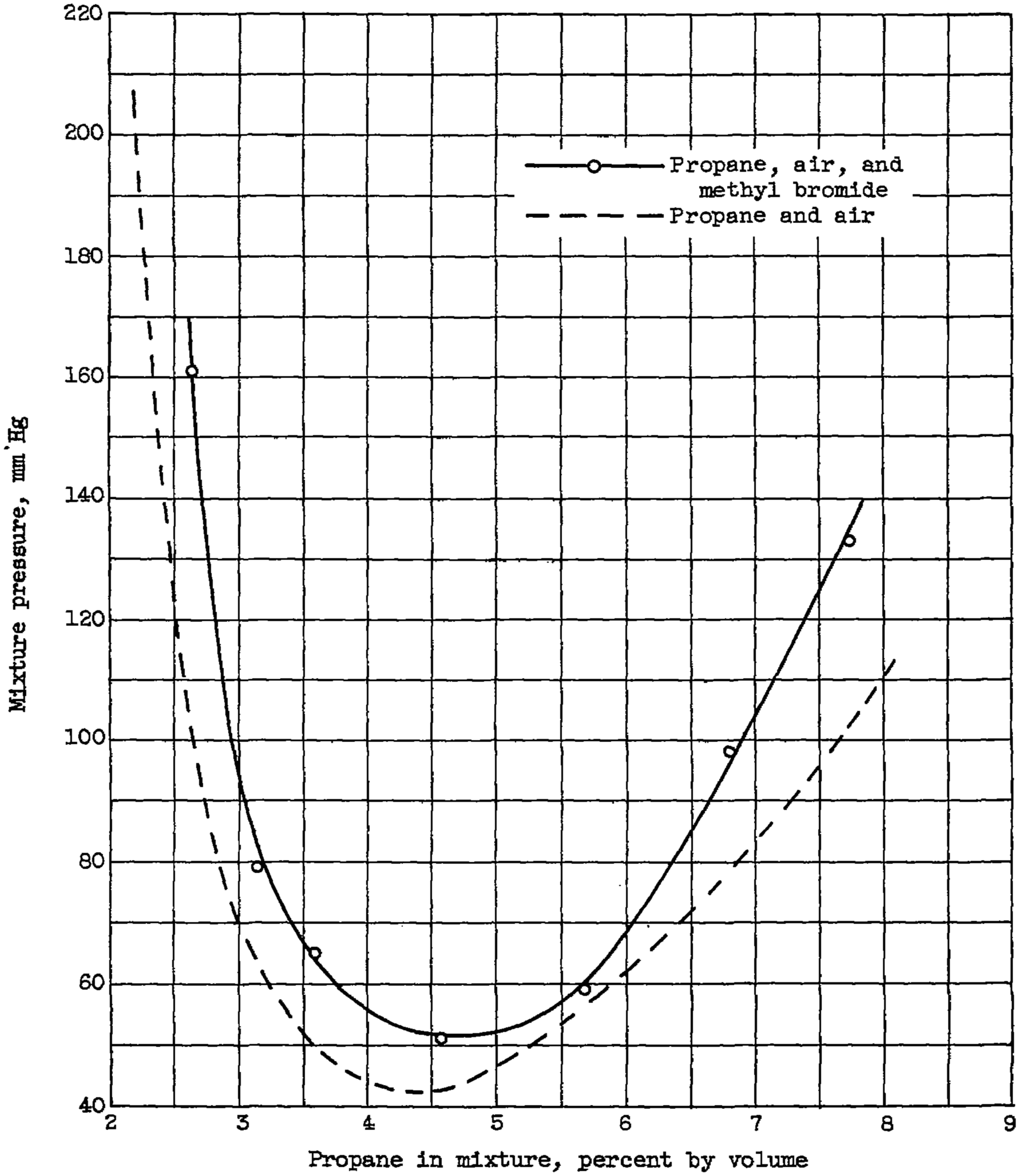
CW-4



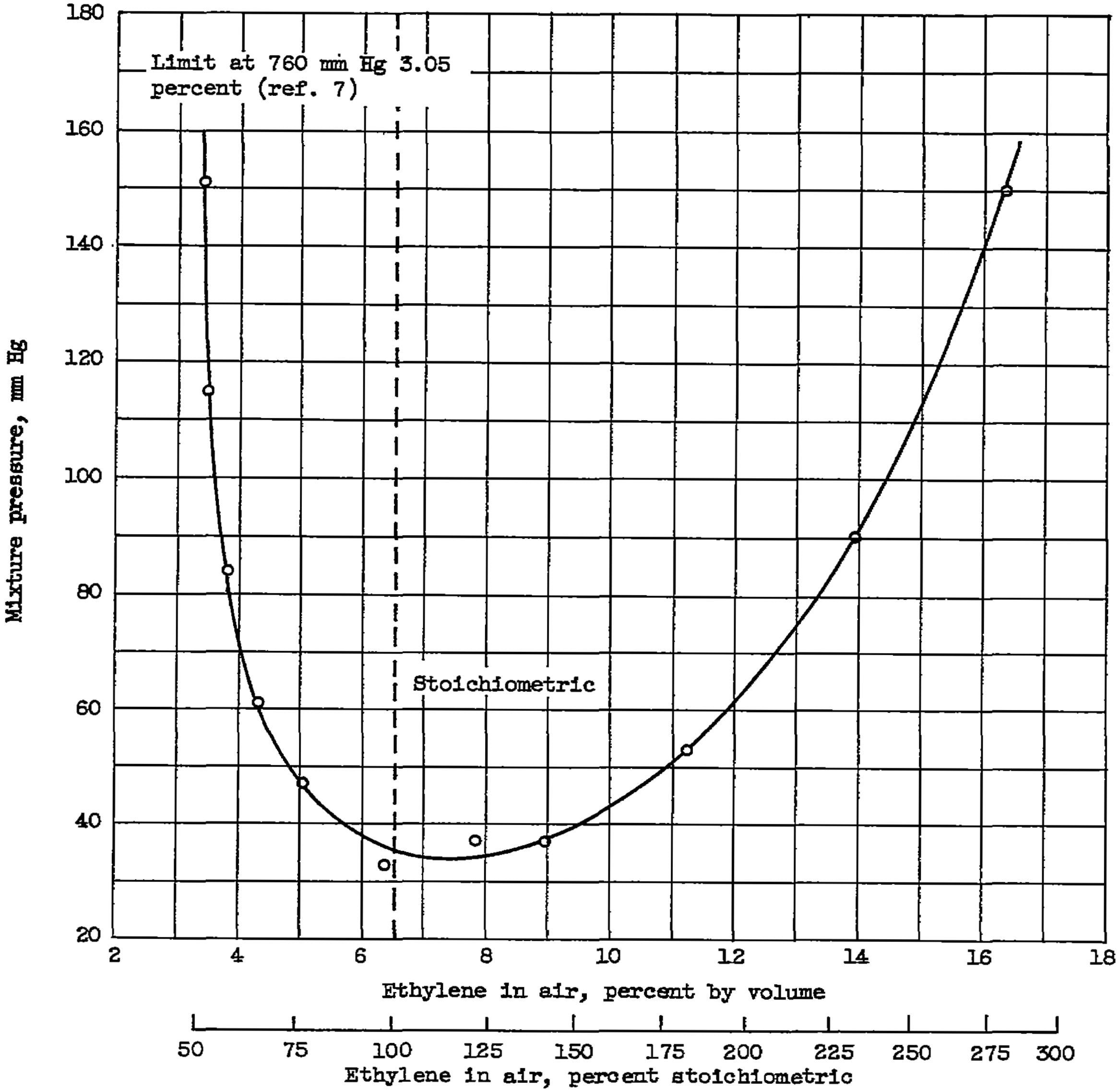
(f) Carbon disulfide, 0.5 volume percent.

Figure 3. - Continued. Effects of additives on low-pressure limits of flame propagation in propane-air mixtures in 3.73-centimeter-diameter tube.



(g) Methyl bromide, 0.5 volume percent.

Figure 3. - Concluded. Effects of additives on low-pressure limits of flame propagation in propane-air mixtures in 3.73-centimeter-diameter tube.



(a) Ethylene-air mixtures.

Figure 4. - Low-pressure limits of flame propagation in additive-air mixtures in 3.73-centimeter-diameter tube.

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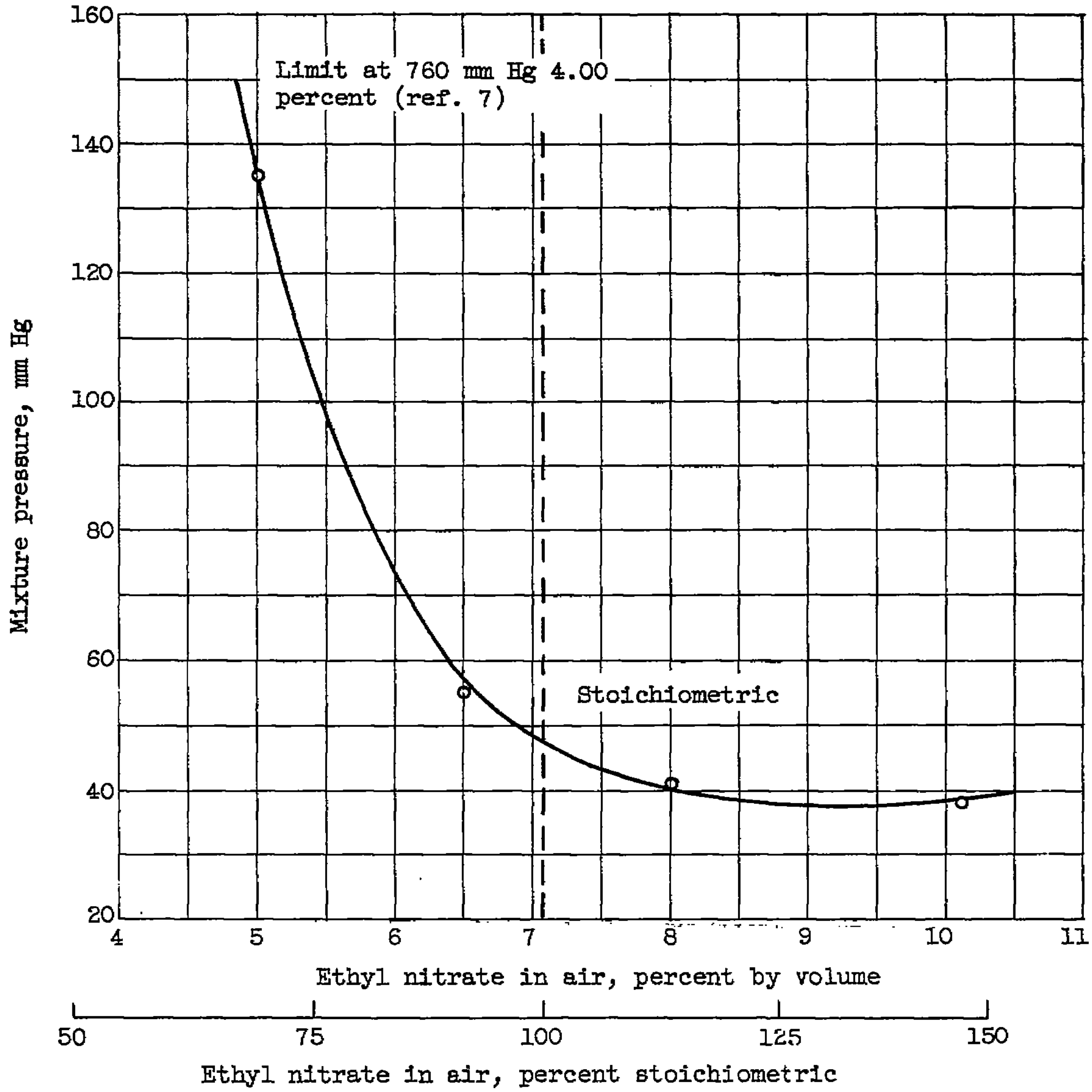

(b) Ethyl nitrate - air mixtures.

Figure 4. - Continued. Low-pressure limits of flame propagation in additive-air mixtures in 3.73-centimeter-diameter tube.

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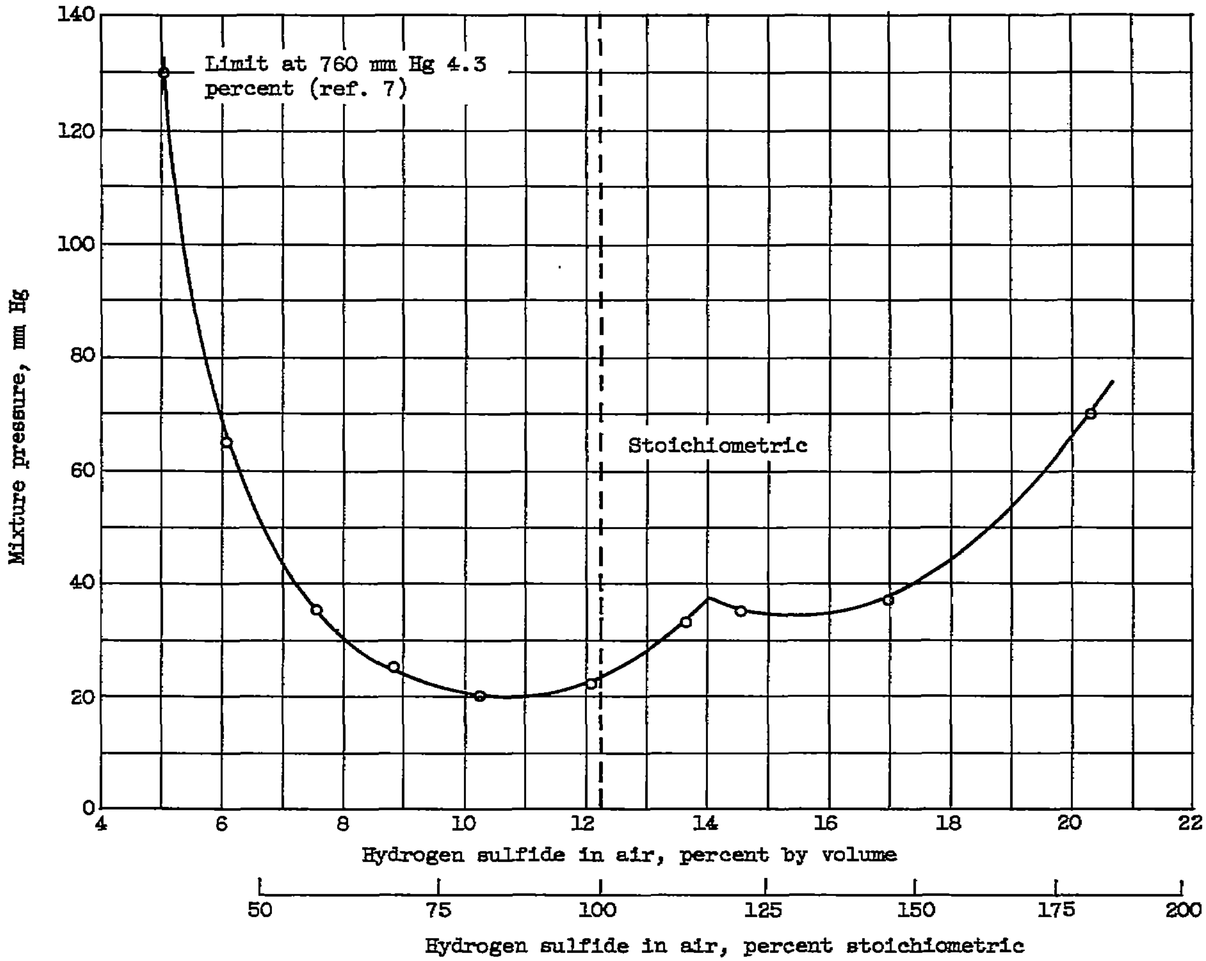

(c) Hydrogen sulfide - air mixtures.

Figure 4. - Continued. Low-pressure limits of flame propagation in additive-air mixtures in 3.73-centimeter-diameter tube.

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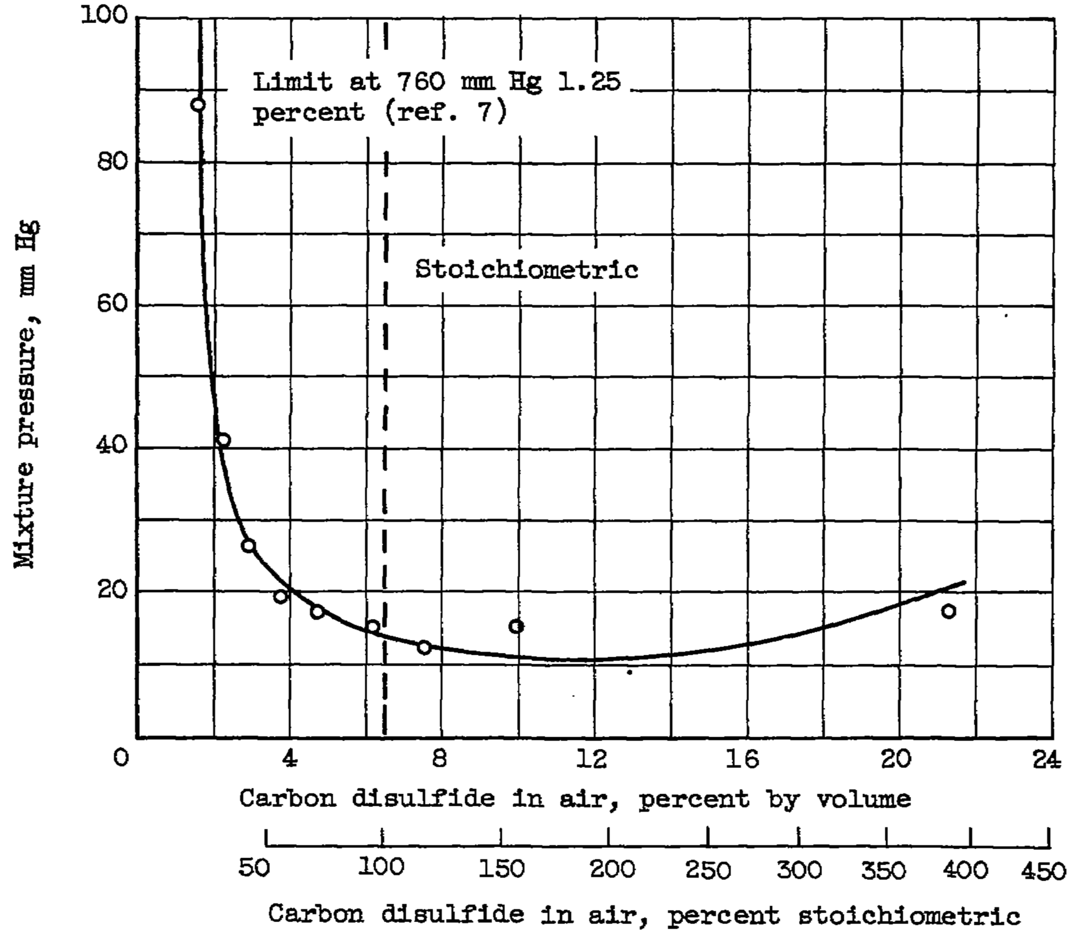

(d) Carbon disulfide - air mixtures.

Figure 4. - Concluded. Low-pressure limits of flame propagation in additive-air mixtures in 3.73-centimeter-diameter tube.

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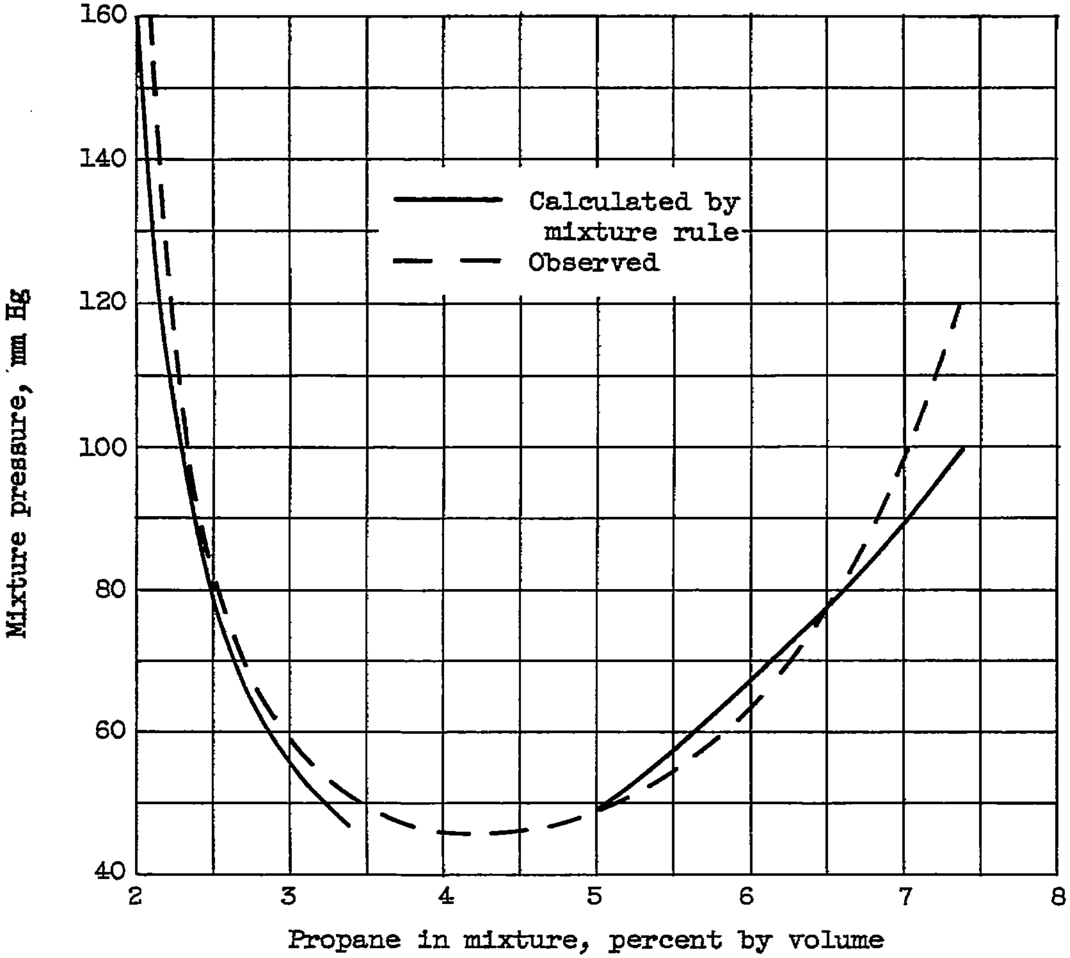
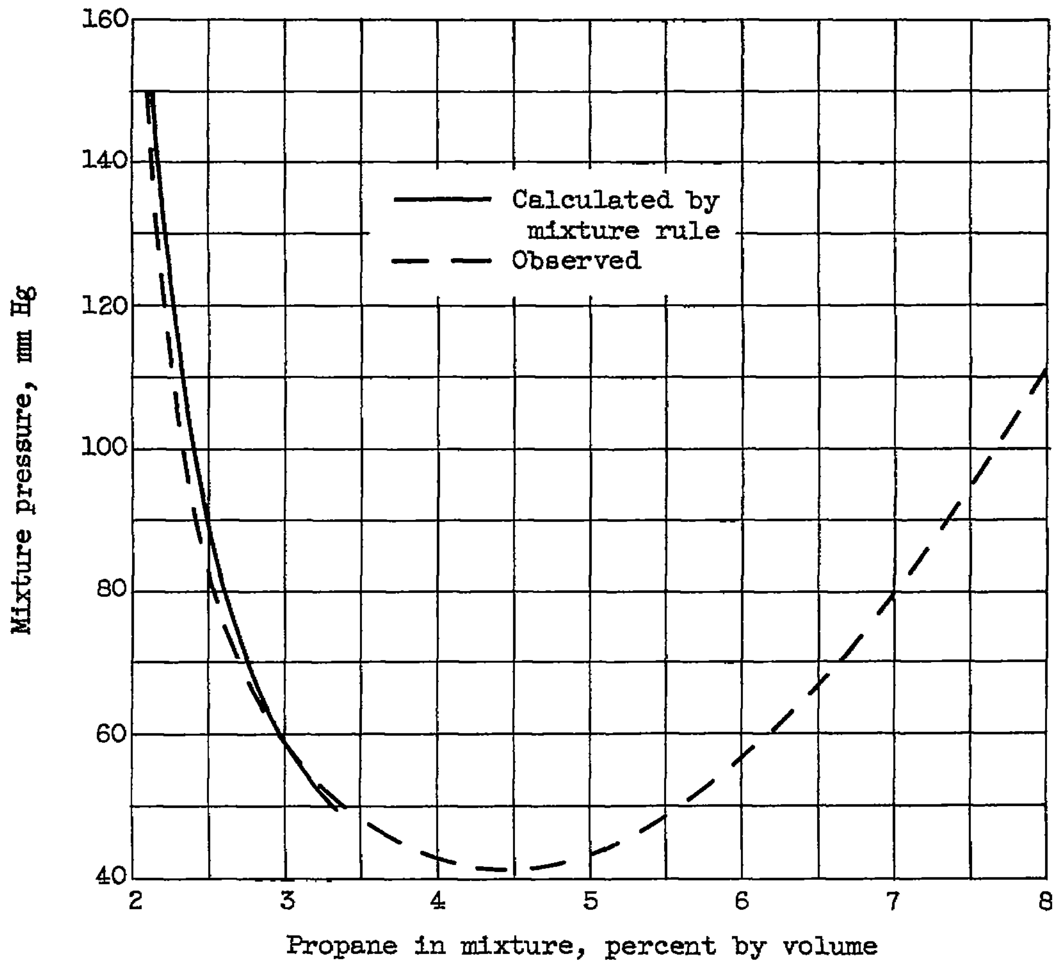


(a) Ethylene, 0.5 volume percent.

Figure 5. - Comparison of calculated and observed pressure limits of flame propagation of mixtures of propane, air, and 0.5 percent additive.



(b) Ethyl nitrate, 0.5 volume percent.

Figure 5. - Continued. Comparison of calculated and observed pressure limits of flame propagation of mixtures of propane, air, and 0.5 percent additive.

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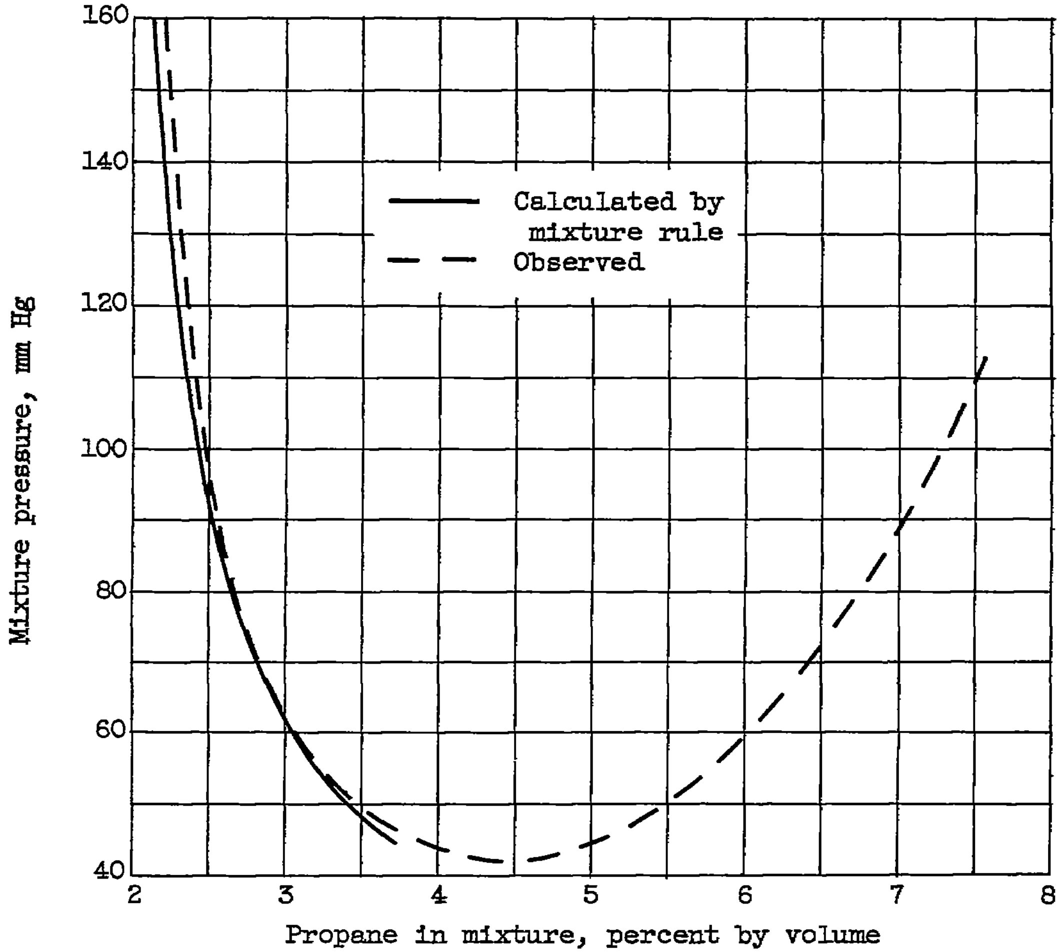

(c) Hydrogen, 0.5 volume percent.

Figure 5. - Continued. Comparison of calculated and observed pressure limits of flame propagation of mixtures of propane, air, and 0.5 percent additive.

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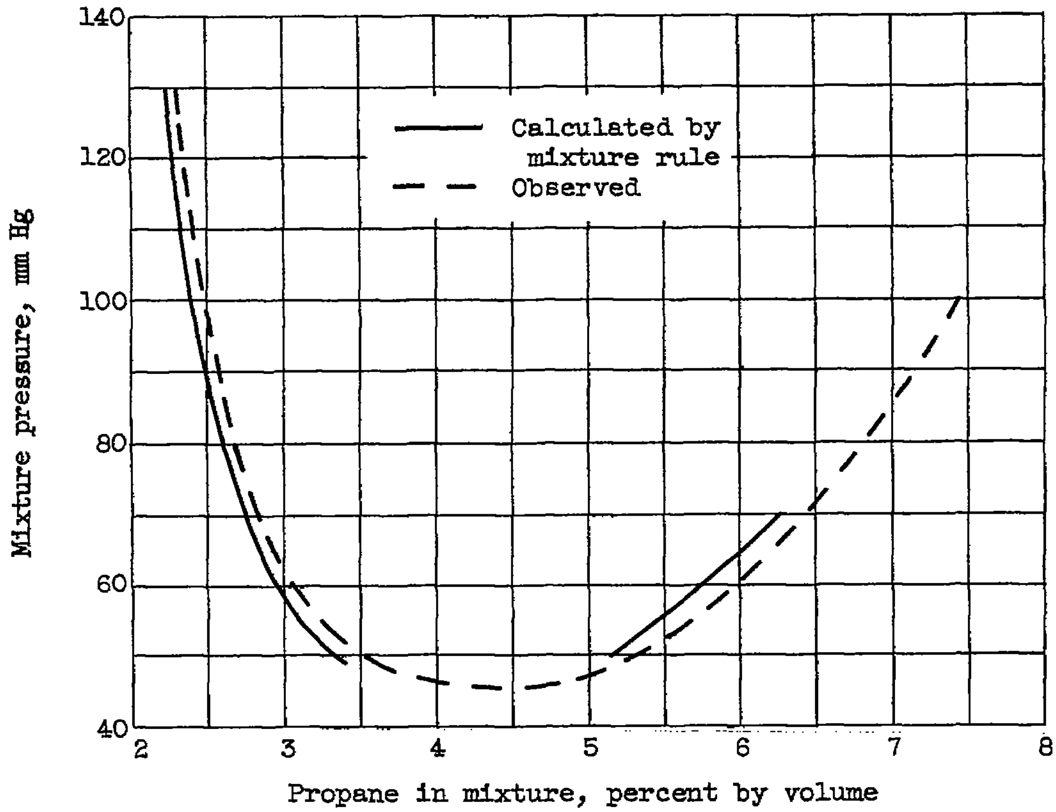

(d) Hydrogen sulfide, 0.5 volume percent.

Figure 5. - Continued. Comparison of calculated and observed pressure limits of flame propagation of mixtures of propane, air, and 0.5 percent additive.

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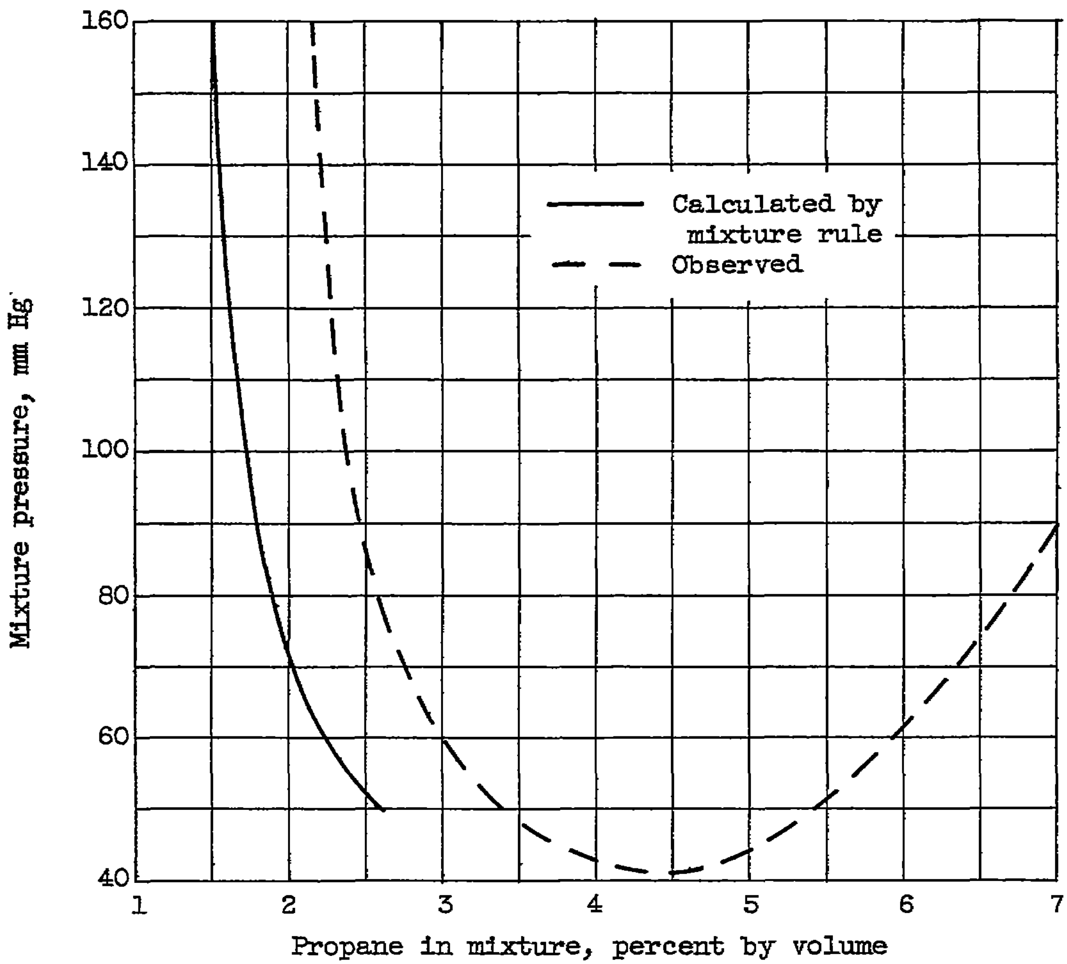

(e) Carbon disulfide, 0.5 volume percent.

Figure 5. - Concluded. Comparison of calculated and observed pressure limits of flame propagation of mixtures of propane, air, and 0.5 percent additive.

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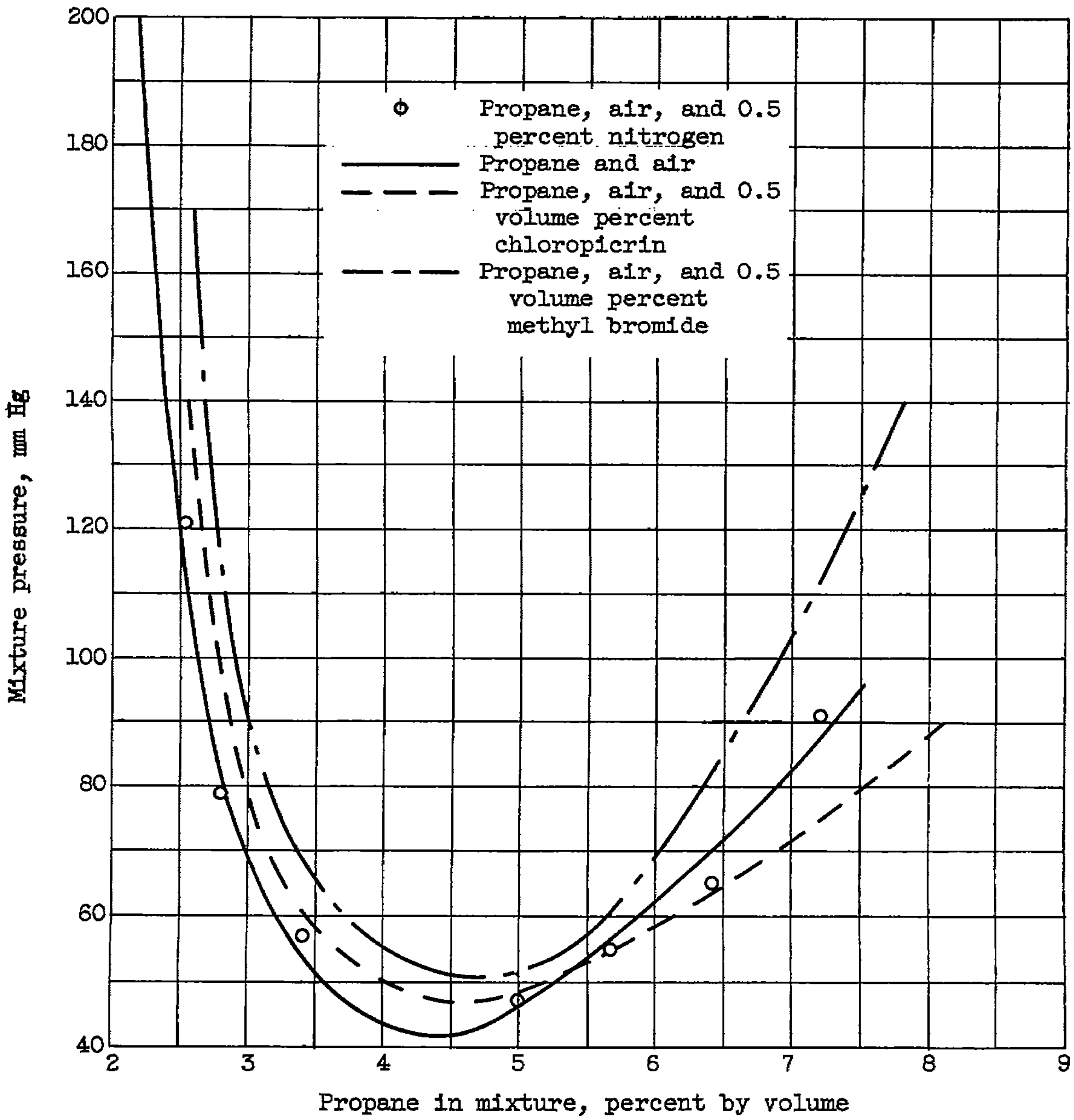

Figure 6. - Effect of 0.5 volume percent nitrogen on pressure limits of flame propagation of propane-air mixtures.